Thermal sigmatropic [1,j] shifts in cyclic systems: a perturbation approach and INDO calculations

Citation for published version (APA):

DOI:
10.1021/ja00444a014

Document status and date:
Published: 01/01/1977

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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Acknowledgment. The authors are grateful to the National Science Foundation and the National Institutes of Health for partial financial support of this research and to Robert W. Strozier and Alex Nicolson for modifications of the computer programs used in this work.

References and Notes

(1) (a) NATO Fellow, 1975; on leave from the University of Pavia, Italy; (b) Camille and Henry Dreyfus Foundation Teacher-Scholar Grant Recipient, 1972-1977; Alfred P. Sloan Foundation Fellow, 1975-1977.


(12) Calculations were carried out by setting matrix elements corresponding to 2p, 2p interactions equal to 0: H. L. Hase and A. Schweig, Tetrathreadon, 29, 1759 (1973).


(17) This type of reasoning was proposed for H2 molecules by C. C. Levin, J. Am. Chem. Soc., 97, 5649 (1975).

(18) NOTE ADDED IN PROOF: Optimizations by 4-31G give the following HCN angles for nitroso benzenes: ylide, 125°; imine, 160°; oxide, 165°.

(19) A planar geometry with a CCO angle of 129° has been found from an STO-3G optimization: G. Leroy, M.-T. Nguyen, and M. Sana, Tetrathreadon, 32, 1529 (1976).

Abstract: Some fundamental aspects of sigmatropic shifts are discussed with the help of INDO calculations and perturbation theory. In cyclic systems the degeneracy of the highest occupied molecular orbital is lifted in the transition state. A suprafacial H shift is determined by a combination of the 1s orbital of the migrating hydrogen with the symmetric MO's of the system and an antarafacial shift by a combination with the antisymmetric MO's. The used perturbation model offers the possibility to reconcile somewhat the concepts of "allowed" and "forbidden". Formally forbidden reactions which, however, have been found experimentally can be explained with this model. Many "forbidden" reactions are in fact "allowed", but they proceed with a higher activation enthalpy. Some transition state geometries have been calculated and the occurring charge transfer is explained in terms of aromaticity.

In 1965 Woodward and Hoffmann postulated their concept of orbital symmetry rules governing pericyclic reactions. 1 In the particular case of sigmatropic reactions, the transition state is thought to be determined by the migrating group and the HOMO or LUMO of the radical-like species left behind, after splitting off the migrating group in thermal and photochemical rearrangements, respectively. In principle, the symmetry properties of the HOMO or LUMO were considered for acyclic polyenes. The major part of the experimental work reported in the last ten years is in agreement with the predictions.

Curiously enough, this applied also to a host of cyclic systems. Whereas the description of acyclic systems is relatively straightforward, cyclic systems have, so far, defied a truly general explanation. The major problem has been the fact that in these systems all but the lowest molecular orbitals are doubly degenerate in the transition state. In 1968 Anastassiou tried to work out the degeneracy problem in C6H15 monocation.2 It was postulated that the presence of the migrating group will disturb the symmetry of the radical, thereby lifting the degeneracy. It was then concluded that the migrating group will combine with the "genuine" HOMO again.

In our opinion, however, the real perturbation is formed by a hydrogen nucleus in the transition state in contrast with Anastassiou's approach in which the perturbation was applied to the reactant. This leads to an entirely different result (see also next section).

There are no compelling reasons to confine the discussion to the HOMO, as already suggested by Berson3 and, in a more elaborate way, by Anh4 and Fukui,5 who worked out the application of perturbation theory to pericyclic rearrangements. The implications of this method have, so far, not been discussed in detail for sigmatropic rearrangements. In general, the nomenclature and selection rules derived for acyclic systems are used without modifications for cyclic polyenes as well.

Here we wish to present evidence that simple perturbation theory allows one to predict several aspects of [1,1] rearrangements in simple systems in a relatively simple fashion. The results are substantiated by INDO calculations. Before specific examples are discussed, it should be realized that a migrating hydrogen, involved in a suprafacial shift, will have to interact with symmetric molecular orbitals. On the other hand, in antarafacial rearrangements the interaction necessarily originates from combination with asymmetric orbitals.
These statements apply to both cyclic and acyclic systems. However, antarafacial shifts in small cyclic systems are only feasible when the hydrogen shifts are along the edge of the ring, i.e., from one carbon atom to a neighboring carbon atom, such as the antara [1,3] and [1,5] shifts in cyclopropene and cyclopentadiene, respectively. In the transition state of these shifts the migrating hydrogen resides in the plane of the ring, a situation in which no interaction with the π system will exist. The only remaining interaction is with the σ framework. In larger rings Möbius arrangements of the polyene fragment are possible, enabling formal antarafacial shifts to occur relatively easy. Möbius-type transition states presumably are also responsible for antarafacial rearrangements in acyclic systems.

For suprafacial rearrangements, the migrating group will interact with a linear combination of molecular orbitals which have a suitable symmetry. For edge-type rearrangements the position of the migrating group may be derived from a simple inspection of the Hückel orbitals. However, in face-type shifts (across the ring) the proper position can only be found by taking recourse to MO calculations. Furthermore, it will be shown that even for shifts in acyclic polyenes molecular orbitals of a cyclic transition state have to be considered. It will also be discussed why some Woodward/Hoffmann "forbidden" reactions occur.

Finally, the limitations of the present approach will be outlined.

Perturbation Treatment

The parameter determining whether or not a particular H shift will occur is the activation enthalpy. We will derive that the activation enthalpy is predominantly determined by the orbital symmetry at migration origin and terminus. We postulate that the following restrictions can be made when considering the transition state: (a) The discussion is confined to the π electrons plus the two electrons of the σ-H bond that is shifting. These electrons participate in the overall conjugation of the system. (b) The π MO's are approximated by the perturbed π MO's of the initial system, the perturbation being the hydrogen nucleus. (c) For the unperturbed π MO's we take the Hückel MO's.

The perturbation treatment consists of two parts: the perturbation of the energy levels and the perturbation of the MO's.

Rayleigh–Schrödinger perturbation theory gives for energy and wave functions:

\[ E_n = E_n^{0} + \langle n^0 | V | n^{0} \rangle + \sum_{m} \frac{\langle m^0 | V | n^{0} \rangle^2}{E_{m^{0}} - E_{n^{0}}} \]  

\[ |n\rangle = |n^{0}\rangle - \sum_{m} \frac{\langle m^0 | V | n^{0} \rangle}{E_{m^{0}} - E_{n^{0}}} |m^{0}\rangle \]

The prime indicates the skipping of \( m = n \). We take as zero-order functions the π MO's of the intermediate state and the 1s orbital of the hydrogen atom. The perturbation is constituted by the interaction between the π MO's and the 1s orbital. This interaction will be appreciable if the orbitals overlap. The first-order correction to the energy \( \langle n^0 | V | n^{0} \rangle \) will be about the same for the different π MO's (and in the same direction), because it arises through the electrostatic effect of the presence of the hydrogen nucleus, without any mixing of orbitals.

The second-order correction to the energy depends on both the interaction element \( \langle n^0 | V | m^{0} \rangle \) and the energy difference \( E_{m^{0}} - E_{n^{0}} \) of the interacting orbitals. The numerator is always positive with the effect that the energy will be lowered/raised depending on whether the perturbing level is higher/lower than the level being perturbed.

The first-order correction to the wave function depends on both the interaction and the energy difference. In fact the only relevant interaction element is:

\[ V_{nm} = \langle m^0 | V | n^0 \rangle = \int \phi_{m^0}(r) \cdot |r_{H} - r|^{-1} \cdot \phi_{n}(r) \, dr \]

where \( r \) is the electron position vector, \( r_{H} \) is the position vector of the hydrogen nucleus, \( \phi_{m^0} \) is the 1s orbital of hydrogen, and \( \phi_{n} \) is the π MO of the system. \( \phi_{m^0} \) will be zero everywhere, except in the neighborhood of the H nucleus. So the p_2 orbitals, where the contribution of the H_1s orbital is dominant, are the p_2 orbitals of the C atoms in migration origin and terminus (for the possible effect of the other p_2 orbitals, see next section). \( V_{nm} \) then becomes:

\[ V_{nm} \approx |c_{n}(C_0) \times |r_{H} - r_{C_0}|^{-1} + c_{n}(C_3) \times |r_{H} - r_{C_3}|^{-1} \]

where \( C_0 \) is the carbon atom at the migration origin, \( C_3 \) is the carbon atom at the migration terminus, \( c_{n}(C_0) \) is the coefficient of \( p_2 \) on atom \( C_0 \), and \( c_{n}(C_3) \) is the coefficient of \( p_2 \) on atom \( C_3 \) in MO \( n \).

In the transition state it follows that \( |r_{H} - r_{C_0}| = |r_{H} - r_{C_3}| \) (symmetrical transition state). Thus \( V_{nm} \) will be maximal when both \( c_{n}(C_0) \) and \( c_{n}(C_3) \) are maximal and of the same sign. Coefficients of equal magnitude but different sign will cause \( V_{nm} \) to be zero. In the transition state the migrating hydrogen will be most involved in the MO which is able to cause the greatest \( V_{nm}/(E_{m^0} - E_{n^0}) \). Qualitative examples will be given in the next section. Quantitative evidence is given by our INDO calculations.

Results

In this section we will present the implications of the use of perturbation theory to some specific examples.

(1) The Cyclopropene System. The Hückel MO's are as depicted below:

\[ \begin{bmatrix} 0.58 & -0.58 & -0.58 \\ 0.58 & 0.58 & -0.58 \\ -0.58 & 0.58 & 0.58 \end{bmatrix} \]

The suprafacial [1,3] H shift from \( C_1 \) to \( C_3 \) is described by the function in which \( \phi_{1s} \) and the symmetrical MO's \( \psi_1 \) and \( \psi_3 \) are involved.

\[ \chi_{\text{supra}} = a_{1s} \phi_{1s} + b_{1s} \psi_1 + c_{1s} \psi_3 \]

where \( \phi_{1s} \) is the 1s hydrogen orbital.

The perturbed energy levels are thus determined by two contributions:

\[ \begin{bmatrix} \]
sition state contains a 2π-electron contribution. The transition state can be described as a hybrid of two configurations, the former of which is aromatic, the latter, too, has an appreciable resonance energy:

\[
\text{[HOMO]} \leftrightarrow \text{[POMO]}
\]

(2) The Cyclopentadiene System. The Hückel MO's are:

In principle, two suprafacial shifts should be considered in this system: (a) a [1,5] shift from C3 to C4; (b) a [1,3] shift from C3 to C2. The former shift will be of the edge type, avoiding overlap with C2 and C4 ("wrong" coefficients in $\psi_2$ and $\psi_3$). The latter shift is of the face type. Perturbation theory predicts the C3–C4 part of the molecule to bend away in the transition state to avoid overlap. This situation corresponds more or less to the transition state that has been calculated by Ustynyuk. However, considering the magnitude of the C3–C4 coefficients and the relatively small interaction with "wrong" carbon atoms, the edge-type rearrangement will be favored. The calculated activation enthalpy for the edge-type transition state is no longer "the HOMO" in an absolute sense. The term POMO (penultimate occupied molecular orbital) is more appropriate. It should be emphasized, however, that in transition states derived from cyclopentadienes with an odd number of double bonds (C$_{4n+1}$H$_{4n+2}$), the HOMO of the cyclopentadiene fragment remains the absolute HOMO in the transition state.

For cyclopentadiene this is illustrated in the next diagram:

\[
\text{[HOMO]} \leftrightarrow \text{[POMO]}
\]

The calculated charge transfer is from the migrating hydrogen to the ring system, which complies again with the aromaticity rules: a transition state containing a 6π-electron contribution.

(3) The Cycloheptatriene System. A consequent and straightforward extension of the perturbational treatment would involve the consideration of a planar C$_7$H$_7$ radical in the transition state. In this situation, the migrating hydrogen in a [1,5] shift cannot sufficiently overlap with both the migration origin and terminus (distance, 3.1 Å). A suprafacial [1,7] shift would not suffer from this difficulty as the optimum distance between the migrating hydrogen and the edge of the ring can always be obtained. The use of (4) in order to predict the relative rates of different sigmatropic rearrangements shows that simple additions of the coefficients of the Hückel MO's are no longer adequate, because of the different distances entering via the $[r_{12} - r_{C}]^{-1}$ term. Starting from the well-known non-planarity of cycloheptatriene in the ground state, a more convenient way to approach the transition state would imply the use of open pentadienyl radical molecular orbitals. These orbitals are as follows:

\[
\text{[HOMO]} \leftrightarrow \text{[POMO]}
\]
The contribution of charge transfer in this system is calculated to be approximately of the migrating hydrogen atom. The comparable fully optimized transition state as calculated for the highest molecular orbital, containing the evidence for this situation is yielded by the geometry of the nonplanar transition state as calculated by the INDO method is given in Figure 3 and Table III. The interaction element between the atoms Ch and C7, which results in the particular MO as depicted. Further evidence for this situation is yielded by the π bond order between the atoms C1 and C7 (or C4 and C5), which is approximately zero.

The Huckel MO's have been given already in the section "cycloheptatriene". Again the [1,5] H shift should be described with the function: $\chi_{\text{supra}} = a\phi_1 + b\psi_1 + c\psi_3 + d\psi_5$

However, it will be difficult to obtain the Möbius transition state in which the C–C bonds must be twisted, if H migration is considered. It can be reached easier in the case of alkyl migration with inversion of the migrating group. The excellent experimental data of Berson show both the alkyl shifts with retention and inversion of configuration. An antara [1,3] H shift can be described by the function: $\chi_{\text{antara}} = a\phi_1 + b\psi_2$

Somewhat to our surprise, INDO calculations on this system yield a picture which deviates in certain aspects from the above mentioned completely open pentadienyl fragment. The symmetries of the various MO's comply with a (homo)cyclopentadienyl rather than an open pentadienyl moiety. In addition, the π bond orders between C1 and C5 are appreciable. The calculations further show that the migrating hydrogen is involved mainly in the POMO, the coefficient for the H 1s function being zero in the HOMO. The electron density on the migrating hydrogen is calculated to be 0.81.

There is no reason to assume that this phenomenon will be restricted to the 1,3-pentadienyl system. In fact, every open 1,3-dienyl system will probably follow this pattern. This conclusion is corroborated quite elegantly by the results obtained for the 1,3-cyclohexadiene system. Even in this case the shift also proceeds via a homocyclopentadienyl transition state as depicted in Figure 4 and Table IV. Electron density on the migrating hydrogen: 0.95.

A similar procedure can be envisaged for larger cycloalka-1,3-dienes. Qualitative predictions regarding relative activation energies are also possible.

In open systems [1,3] antarafacial shifts are to be considered.
as well (vide supra). In 1,3-pentadiene this is described by the function:

\[ \chi_{\text{antara}} = a\psi_1 + b\psi_2 + c\psi_4 \]

In order to enable this shift, the pentadiene fragment will be forced into a Möbius arrangement. As a consequence, positive overlap is only possible with asymmetric subjacent molecular orbitals. This, in turn, will decrease the interaction elements because of the increased energy difference between the polyene molecular orbitals and the hydrogen Is function, as compared with the suprafacial case. The result is that the activation enthalpy of the antarafacial shift is considerably higher than for the suprafacial shift. Both activation enthalpies have been calculated by Bingham and Dewar: 28.3 kcal/mol for the suprafacial [1,5] H shift in 1,3-pentadiene, and 37.0 kcal/mol for the antarafacial [1,5] H shift in the same system.\(^9\)

**Discussion, Scope, and Limitations**

The literature on sigmatropic shifts reveals several examples of nominally “forbidden” rearrangements which nevertheless occur.\(^10\) On the other hand, some “allowed” shifts have never been observed. The present perturbation treatment sheds more light on these phenomena. An “allowed” transition state can be hampered by the absence of a suitable (from a symmetry viewpoint) molecular orbital within a reasonable energy distance from the orbital of the migrating group. Further, interaction of the migrating group with subjacent orbitals of the \(\pi\) moiety might assist a migrating group in following a “forbidden” pathway, as already pointed out by Berson:\(^5\)

![Diagram](image)

In a similar way “forbidden” antarafacial shifts are possible in a Möbius arrangement via asymmetric orbitals (the symmetric orbitals have a negative overlap in this Möbius arrangement), for example, the antarafacial [1,5] H shift in 1,3-pentadiene.

The present treatment shows that even in formally allowed transitions subjacent molecular orbitals are involved in the determining MO of the transition state.

Another interesting aspect of the method is the possibility of predicting molecular conformations in the transition state from simple inspection of the Hückel MO’s. Molecular parts with “wrong” signs of the coefficients will tend to avoid overlap with the migrating group. This was demonstrated in cyclohexadiene and cycloheptatriene where our calculations show that those parts of the framework bend away from the migrating group.

Quite obviously, the complexity of the molecular orbitals and the accompanying possibilities of combination grow rap-

**Table IV. The Transition State Geometry of the Cyclohexadiene System**

<table>
<thead>
<tr>
<th>Distance, Å</th>
<th>Angle, deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_1)-C(_2)</td>
<td>1.43</td>
</tr>
<tr>
<td>C(_2)-C(_3)</td>
<td>1.39</td>
</tr>
<tr>
<td>C(_3)-C(_4)</td>
<td>1.48</td>
</tr>
<tr>
<td>C(_4)-C(_5)</td>
<td>1.77</td>
</tr>
<tr>
<td>C(_5)-C(_6)</td>
<td>2.33</td>
</tr>
<tr>
<td>C(_6)-C(_7)</td>
<td>1.13</td>
</tr>
<tr>
<td>C(_7)-C(_8)</td>
<td>1.12</td>
</tr>
<tr>
<td>C(_8)-C(_9)</td>
<td>1.12</td>
</tr>
<tr>
<td>C(_9)-C(_10)</td>
<td>1.13</td>
</tr>
<tr>
<td>C(_10)-C(_11)</td>
<td>1.12</td>
</tr>
<tr>
<td>H(_5)=S</td>
<td>0.95</td>
</tr>
</tbody>
</table>

| \(\alpha\) | 100.6° |
| \(\beta\) | 65.5° |
| \(\gamma\) | 5.0° |

In principle, several shifts are possible in this system. Considering symmetry and coefficients, for example, shifts are possible via \(\psi_3\) and \(\psi_5\) from \(C_1\) to \(C_7\) or via \(\psi_4\) from \(C_1\) to \(C_5\).

Meaningful predictions are difficult to make. In cases like this the more sensible approach will be to take recourse to INDO calculations right from the start. The perturbation theory combined with the Hückel orbitals will now serve mainly to indicate logical starting points. For example, a [1,5] H shift in 1,3,5-heptatriene will require a transition state as follows, in which interaction with the lone double bond might occur:

![Diagram](image)

On the other hand, a [1,7] shift will require a homocycloheptatrienyl system. In order to determine which shift will be favored, the respective transition states of different pathways will have to be compared by way of INDO calculations. The suprafacial [1,7] H shift will be a hydride-like shift, comparable with the suprafacial [1,3] H shift in cyclopropene. The difference in absolute magnitude of the charge transfer calculated for the cyclopropenyl and cycloheptatrienyl systems seems relevant and is to be ascribed to the difference in ionization potentials. This way of comparing charge transfers is similar to the use of differences in electron affinities between the cyclopentadienyl, homocyclopentadienyl, and open pentadienyl systems.\(^5\)

Another very obvious extension of the present approach is the treatment of homogenous catalysis of rearrangements by transition metals. Two possibilities are to be distinguished: acceleration of allowed transitions and transformation of forbidden rearrangements into allowed ones. By interaction of the migration framework with the metal, the orbitals of both
will be affected. As a result, also the interaction terms with potential migrating groups will be altered.

Recently, a similar theory of catalytic activity has been worked out.11

References and Notes

(1) (a) R. B. Woodward and R. Hoffmann, J. Am. Chem. Soc., 87, 395 (1965); (b) ibid., 87, 2046 (1965); (c) ibid., 87, 2511 (1965).


(10) (a) G. R. Krow and J. Reilly, J. Am. Chem. Soc., 87, 3837 (1975); (b) see R. K. Lustgarten and H. G. Richey, Jr., ibid., 86, 6595 (1974), and ref 54–56.


(12) The experimental and theoretical activation enthalpies are in good agreement. See ref 8.

(13) The geometry of the cyclopentadiene transition state has been optimized with respect to eight variables (see Table II). A fully optimized transition state as calculated by Ustynyuk et al. shows no essential difference. Our optimization resulted in an approximately symmetric structure as can be derived from Table II, which shows only approximately equal to γ and β = ρ. Consequently for all other cyclic systems the symmetry plane was assumed, while optimizing all other variables. In all systems it was assumed that the transition state has only one negative force constant.

(14) The reason for the cyclic symmetry properties in the present case is probably to be ascribed to the enhanced flexibility of the system. This enables a closer approach between migration origin and terminus in the transition state as compared to cycloheptatriene. In the acyclic pentadiene system, the p3 orbitals of migration origin and terminus overlap in order to form a partial π bond. In the cycloheptatriene system, the two carbon atoms involved are held apart by the rather rigid ethylene moiety.

(15) NOTE ADDED IN PROOF. In reality the H2+ level lies about 1.3 (β = -2.4 eV) below the zero level, but this does not affect any of the conclusions.

Global Topology of Triatomic Potential Surfaces

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Abstract: A new coordinate system for describing triatomic molecules is introduced. Within this coordinate system various topological features of importance are discussed. Particular emphasis is placed on the Jahn-Teller theorem and the resulting branch-cuts on the potential surface.

Potential surfaces are of importance in chemistry for explaining geometry, spectra, and chemical reactions. Triatomic potential surfaces (especially for excited states) have recently become of even greater interest because of work in plasmas, lasers, and atmospheric pollution associated with various aspects of the energy crisis. Unlike diatomic molecules which are fairly well characterized, polyatomic potential surfaces are only vaguely understood. While the general features expected for a diatomic molecule potential curve over the whole range of possible molecular conformations are well known, such a global topology for triatomic molecules is not usually discussed.

General Considerations

A potential surface, for the purpose of the present discussion, will be a function $U(X_1, \ldots, X_K)$ generated as one of the solutions to an electronic (Born-Oppenheimer) Schrödinger equation

$$H\psi(r_1, \ldots, r_N; X_1, \ldots, X_K) = U(X_1, \ldots, X_K)\psi(r_1, \ldots, r_N; X_1, \ldots, X_K) \quad (1)$$

where the $r_i$ are electronic coordinates and the $X_i$ are coordinates for describing the conformation of the nuclei in the molecule. The operator $H$ in the simplest approximation is just the usual electronic hamiltonian involving electronic kinetic energy and coulomb interactions,

$$H = -\frac{\hbar^2}{2m} \sum X_i^2 - e^2 \sum \sum_{A \neq B} Z_A Z_B r_{AB}^{-1} + e^2 \sum_{i,j} r_{ij}^{-1}$$

For discussing a potential surface $U$ it is sufficient to pick the complete set of coordinates $X_i$ which affect the shape or size of the molecule but not its position or orientation in space. Hence for three or more atoms $K$ is $3N - 6$ where $N$ is the number of atoms (for a general discussion of $U$ the question of whether the molecule is "linear" or not does not enter).

Accordingly for all cyclic systems the transition state has only one negative force constant.

The reason for the cyclic symmetry properties in the present case is probably to be ascribed to the enhanced flexibility of the system. This enables a closer approach between migration origin and terminus in the transition state as compared to cycloheptatriene. In the acyclic pentadiene system, the $p$ orbitals of migration origin and terminus overlap in order to form a partial $\pi$ bond. In the cycloheptatriene system, the two carbon atoms involved are held apart by the rather rigid ethylene moiety.

NOTE ADDED IN PROOF. In reality the $H_2^+$ level lies about $1.3 (\beta = -2.4 \text{ eV})$ below the zero level, but this does not affect any of the conclusions.